(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 461 834 A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 91305202.3

(51) Int. Cl.[5]: G11B 5/64, G11B 5/72

(22) Date of filing: 10.06.91

(30) Priority: 11.06.90 JP 151955/90
19.11.90 JP 313519/90
19.11.90 JP 313521/90

(43) Date of publication of application:
18.12.91 Bulletin 91/51

(84) Designated Contracting States:
DE FR GB IT NL

(71) Applicant: MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD
1006, Oaza Kadoma, Kadoma-shi
Osaka 571 (JP)

(72) Inventor: Torii, Hideo
1-9-18, Nishikounoike-cho
Higashiosaka-shi, Osaka-fu 578 (JP)
Inventor: Fijii, Eiji
2-4-11, Shimizu, Asahi-ku
Osaka-shi, Osaka-fu 535 (JP)
Inventor: Hattori, Masumi
1-chome, 25-3, Kouhoku
Hirakata-shi, Osaka-fu 573 (JP)
Inventor: Aoki, Masaki
7-21, Aogein
Minou-shi, Osaka-fu 562 (JP)
Inventor: Kuribayashi, Kiyoshi
590-1, Matsudome, Uenohara-cho
Kitatsurugun, Yamanashiken 409-01 (JP)

(74) Representative: Crawford, Andrew Birkby et al
A.A. THORNTON & CO. Northumberland House 303-306 High Holborn
London WC1V 7LE (GB)

(54) A magnetic recording medium and its manufacturing process.

(57) A magnetic recording medium, comprising; a 2-layer film formed on a glass disk substrate as an under layer composed of an amorphous oxide or NaCl oxides like a NiO or CoO and the like, or any soft magnetic oxide of Mn-Zn ferrite, Ni-Zn ferrite and the like, or a combination of those 2 materials; a magnetic recording medium formed thereon composed of a Co ferrite perpendicular magnetic film of a columnar structure; and a structure formed thereon with a lubricant layer medium. This magnetic recording medium is used for a magnetic rigid disk apparatus. The substrate is made by press-molding the glass plate at a high temperature. The under layer film and Co ferrite film are composed of vapors of organic material compounds and oxygen as their raw materials, and made by a plasma assisted CVD method.

EP 0 461 834 A2

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a magnetic recording medium and its manufacturing process which makes high density magnetic recording possible.

1. Description of the Prior Art

Magnetic recording medium is now widely used in a form of tapes for audio equipment and video recorders, or in a form of disk like a floppy disk and a magnetic rigid disk. In the latest highly-developed intelligent society, the volume of information to be stored are increasing year by year, therefore, the demand for a larger storage unit and higher density are also increasing. For example, in a magnetic rigid disk unit as used for computer peripheral units, a trend toward both a larger volume and a smaller volume is shown year by year, furthermore, development toward higher density and smaller sign are also being developed for a magnetic rigid disk used for a magnetic rigid disk unit. With the increasing demand toward higher density, the recording medium materials used for the magnetic rigid disk have also changed. The magnetic recording medium as conventionally used has been an application-type medium which was made by applying a needle-shape magnetic powder together with an organic binder. Recently, instead of using the above methods, a thin film-type medium was placed on the market and has widely been used which was made by directly forming magnetic film without using an organic binder on a disk substrate, through the use of such means as plating as well as vacuum sputtering methods. Concretely, instead of using an application-type magnetic rigid disk which is applied with the needle-shape magnetic powder of gamma iron oxide onto an aluminum disk substrate, a rigid magnetic disk of Co-Ni/Cr alloy thin film has come to be in wide use.

Now, as one example of a magnetic rigid disk used with the existing Co-Ni/Cr alloy thin film, explanation follows below of the structure and its production method of the thin-film magnetic rigid disk made by means of the vacuum spattering method. First of all, an aluminum circular disk mirror polished as a disk substrate is prepared. On its surface, a Ni-P film of about 20 μ m is formed by the plating method. Then, the surface is polished up. In this instance, a texture is made on the surface. Then, Cr thin film of about 0.1 μ m thick is made by a vacuum sputtering method with a Co-Ni thin film (less than about 0.008 μ m formed as a magnetic layer. Here, as the Co-Ni thin film of th magnetic layer itself al ne has such a problem in corrosion resistance as oxidation, a protective film layer (about 500 - 800 Å) of SiO_2 or amorphous carbon and the like are formed for a purpos of improving th corrosive resistance. Furthermore, a coating layer (about 100 - 500 Å) of lubricant is formed on th ' surface, and then a magnetic rigid disk of Co-Ni/Cr alloy thin film is built up.

Namely, the magnetic rigid disk structure of Co-Ni/Cr alloy thin film is composed of 6 layers of "lubricant layer / protective layer / Co-Ni alloy magnetic layer / Cr layer / P plating layer / Aluminum substrate". However, this structure has such an inherent disadvantage as making the production process more complicated.

Also, as the aforementioned magnetic rigid disk is of longitudinal recording medium, an effort to further increase the recording density for shorter recording wave length makes the recording difficult due to influence from a magnetic field. Therefore, as a magnetic recoding medium by means of a perpendicular recording system which improved the above-mentioned disadvantage, a study was widely made for a Co-Cr thin film medium on a method for record reproduction by which a magnetic head makes contact with the medium without lifting the magnetic head itself.

This Co-Cr alloy thin film medium has such a disadvantage as being easily subject to scars against sliding of the magnetic head. As the Co-Cr alloy thin film is a metal thin film, in a same manner as Co-Ni / Cr alloy thin film, there is also a problem in corrosion resistance for oxidation, and, therefore, for the Co-Cr alloy thin film medium, there has been such a great problem as assuring reliability for improving passware endurance and corrosion resistance.

Various schemes were made to solve this problem. One of them is a method to provide a protective layer of amorphous carbon on a Co-Cr thin film surface. In addition, a method to provide a protective layer of cobalt oxide on the Co-Cr thin film surface is contrived.

In this manner, efforts are being made for improving the reliability in endurance and corrosion resistance in passware, by building up a coating film on the surface of Co-Cr alloy thin film medium.

In a magnetic rigid disk device, making a running height (flying height) as low as possible for the magnetic disk of magnetic head will lead to improvement of the recording density owing to a decrease in an output of loss (spacing loss) due to spacing, i.e, an interval between magnetic head and magnetic disk. For lowering a flying height, excellent smoothness is required for a substrate surface for protecting the magnetic head from crashing. With the conventional disk substrate, almost all are used with aluminum substrates. However, the aluminum substrate has a limitation in a processing accuracy to obtain the adequate surface smoothness, thus has been difficult to improve the smoothness. In this

connection, glass substrates which are easy to get processing smoothness are nowadays thought to be effectiv in terms of material and th n began to be in use. However, the glass substrates have such a disadvantage of being expensive compared with aluminum substrates due to complexity of production process.

Recently, in order to make the high recording density possible, running at a flying height volume of about 0,05 - 0,1 μ m is considered to be necessary.

However, there are problems of changes in properties resulting from oxidation and the like in any of the afore-mentioned Co-Ni / Cr thin film medium or Co-Cr thin film medium, which needs a protective film layer for the purpose of promoting the corrosion resistance. In this sense, once a protective film layer is provided, an interval between a magnetic recording medium (magnetic layer) and a magnetic head is, in terms of magnet, widened by a thickness of the protective layer even if the flying height comes to smaller, which resulted in an increase in spacing loss and has thereby kept a move toward a higher density from coping therewith. Besides, formation of-the protective film has increased a number of production processes of the medium and thus has made the process complicated.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a magnetic recording medium in a magnetic rigid disk form which is, like a conventional alloy magnetic thin film disk, excellent in reliability without need of a protective layer and has a component of perpendicular magnetic recording capable of complying with high density magnetic recording, and also its production method.

In order to achieve the aforementioned object, the present invention is not a magnetic recording medium composed of an alloy (metallic) magnetic thin film medium material which needs a conventional protective film layer, but is a magnetic recording medium using a magnetic recording medium material of an oxide thin film containing such a chemical composition as iron and cobalt, having a perpendicular recording component capable of recording with higher density compliance and a columnar structure which consists mainly of an oxide of a spinel crystal structure; and the thin film of the medium is formed on a glass substrate via a different kind of oxide thin film on a under layer film and also on its surface a lubricant layer is formed, thus making a magnetic recording medium in magnetic rigid disk form of a film structure. Besides, th present inventi n is a glass disk substrate manufacturing process made by heating a glass material and press molding, a thin film forming process for an oxide magn tic recording material obtained by a plasma enhanced MO-CVD method and an oxide material for its under layer film, and a production method of aforementioned magnetic recording medium produced through a lubricant film layer forming process by lubricant application. The inventors have found out a production method for a thin film of magnetic oxides capable of being used as a magnetic recording medium through use of plasma enhanced MO-CVD method by using a MO raw material (organic metal raw material) which represents β - diketone complex such as metal acetylacetonate like iron, cobalt and the like. (M. Aoki et. al., USP4717584)

Furthermore, by controlling the film forming conditions of plasma enhanced MO-CVD method, a perpendicular magnetized thin film can be obtained which consists of a spinel oxide magnetic body only whose form is of minute columnar grains densely grown onto the under layer substrate. (H. Torii et. al., USP4975324, and E. Fujii et. al., IEEE Translation Journal on Magnetics in Japan, vol, 4, No. 8, p512 - 517 (1989))

The film material thus obtained is an oxide material having a spinel crystal structure, the same material as magnetic ceramics called in general ferrite. Since the ferrite is an oxide ceramic, it is not only excellent in acid resistance but also in weatherability with sufficient hardness. Therefore, a magnetic recording medium thin film of spinel oxides as used in the present invention is likewise a magnetic recording medium thin film having excellent characteristics in acid proofness, weatherability and wear resistance. Therefore, as a protective film layer is not required for the purpose of protecting the magnetic thin film required for the conventional alloy magnetic recording medium thin film material in terms of forming the film when magnetic rigid disk is adopted, a loss of head output (spacing loss) by spacing is noticeably reduced, as an interval (spacing) between a running magnetic head and magnetic recording medium thin film can be directly and effectively made small by making a flying height small for high density recording compliance,thereby larger capacity magnetic rigid disk can be made. Besides, the film structure of magnetic rigid disk becomes simple.

Furthermore, as the magnetic recording medium thin film as used for the present invention has a perpendicular magnetic component, influence of decreasing magnetic field can be reduced for the short wave recording for higher density recording.

Here, for the oxide thin film magnetic recoding medium of thin film which contains such a chemical components as iron and cobalt, the use of different kind of oxide thin film as a under layer film helps mak th control for crystal ori ntation and columnar diameter of columnar structure grains remarkably easy, and the magnetic recording characteristics is als improved. Yields on better products can also be

improved in the production.

As the use of a method, so called, a plasma enhanced MO-CVD m thod enables the oxid thin film of under layer film and oxide magnetic thin film to be continuously formed even with changing the gas of raw material, formation of multi-structured oxide thin film can be easily made even on the glass disk substrate. Therefore, as mentioned earlier, compared with a magnetic rigid disk of the conventional alloy magnetic material of complicated film structure (6-layer structure), a magnetic recording medium of remarkably simple film structure can be made which is a magnetic disk form of "lubricant layer / oxide magnetic thin film layer / glass substrate of thin oxide under film layer".

The inventors also found in the past a method to produce a disk type glass substrate by press forming the glass block material with heat through use of a pair of press dies. (M, Aoki et, al., USP4953385). This is a remarkably process-saving production method compared with the magnetic recording medium production method of a magnetic rigid disk form of alloy magnetic material which represents the conventional Co-Ni / Cr alloy magnetic disk, adopting a process, in which a glass disk substrate to be used for the magnetic recording medium of the present invention is made with heat through a press molding method by first heating a glass block material using a pair of press dies, and then on the disk substrate thus being made and left as it is an aforementioned under layer thin film and a magnetic thin film are continuously formed through the plasma enhanced MO-CVD method and a lubricant layer is further made by applying the lubricant to the surface thereof.

With the above structure, the magnetic rigid disk of the film structure of the present invention is, when a flying height of the magnetic head becomes lowered, able to get a high head output even at a short wave area compared with the conventional alloy magnetic rigid disk, thus making it possible to cope with the higher density recording and a larger capacity of a magnetic rigid disk device. Also, the film structure is simple compared with the alloy disk structure, and according to the production process of the present invention the production process can also be remarkably reduced. That is, saving steps of processes allows the supply of magnetic recording medium capable of coping with higher density recording to be made with a lower cost compared with the conventional process.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows an enlarged secti nal view of main area of th magnetic recording medium of a magnetic rigid disk form as referred to the embodiment 1 of the present invention.

Fig. 2 shows a schematic diagram of a press machin for glass material as referred to the embodiment 1 of the present invention.

Fig. 3 shows a schematic sectional levations view of a plasma CVD apparatus used for making a magnetic film and its under layer film as referred to the embodiment 1 of the present invention.

Fig. 4 shows a comparison diagram of an output voltage characteristics made by a magnetic head for the magnetic recording medium as referred to the embodiment 1 of the present invention, medium without under layer film, and a conventional medium for comparison.

Fig. 5 shows an enlarged sectional view of the main area of the magnetic recording medium of a magnetic rigid disk form as referred to the embodiment 2 of the present invention.

Fig. 6 shows a comparison diagram of an output voltage characteristics made by a magnetic head for the magnetic recording medium as referred to the embodiment 2 of the present invention medium without under layer film, a conventional medium for comparison.

Fig. 7 shows an enlarged sectional view of the main area of the magnetic recording medium of a magnetic rigid disk form as the embodiment 3 of the present invention.

Fig. 8 shows a comparison diagram of an output voltage characteristics made by a magnetic head for the a magnetic recording medium as referred to the embodiment 3 of the present invention medium without under layer film, and a conventional medium for comparison.

Fig. 9 shows an enlarged sectional view of the main area of the magnetic recording medium of a magnetic rigid disk form as referred to the embodiment 4 of the present invention.

Fig. 10 shows a comparison diagram of an output voltage characteristics made by a magnetic head for the medium between a magnetic recording medium as referred to the embodiment 4 of the present invention medium without under layer film, and a conventional medium for comparison.

Fig. 11 shows an enlarged sectional view of the main area of the magnetic recording medium of a magnetic rigid disk form as referred to the embodiment 5 of the present invention.

Fig. 12 shows a comparison diagram of an output voltage characteristics made by a magnetic head for the a magnetic recording medium as referred to the embodiment 5 of the present invention, medium without under layer film, and a conventional medium for comparison.

1 ... glass disk substrate 2 ... CoZnF amorphous oxide film
3 ... Co ferrite film 4 ... Lubricant layer
5 and 6 ... press dies 7 ... Raw material glass circular disk
8 and 9 ... heater for a press dies

10 ... supply jig for a raw material glass circular disk
11 ... piston cylinder for an upper die
101 ... piston cylinder for a lower die
102 ... preheating tunnel furnace
103 ... inlet for taking out a disk
12 ... reaction chamber 13 ... electrode
14 ... exhaust system
15 ... high frequency wave power source
16, 17, 18, 19 and 20 ... vaporizer
21, 22, 23, 24 and 25 ... first valve
26, 27, 28, 29 and 30 ... second valve
31 ... carrier gas cylinder 32 ... reactive gas cylinder 33 ... heater for substrates
34 ... Co ferrite/CoZnFe amorphous oxide magnetic record ing medium
35 ... Co-Ni/Cr alloy thin film medium
36 ... Co ferrite monolayer medium
37 ... NiO film
38 ... Co ferrite/NiO magnetic recording medium
39 ... Mn-Zn ferrite film
40 ... Co ferrite/Mn-Zn ferrite magnetic recording medium
41 ... Co ferrite/Mn-Zn ferrite/CoZnFe amorphous oxide magnetic recording medium
42 ... Co ferrite/Mn-Zn ferrite/NiO magnetic recording medium

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Embodiment 1

Explanation for one embodiment of the present invention follows below with reference to drawings.

Fig. 1 shows a structure of magnetic recording medium in the embodiment of the present invention, in which numeral 1 represents a glass disk substrate, numeral 2 represents a CoZnFe amorphous oxide film layer, numeral 3 represents a Co ferrite film, and numeral 4 represents a lubricant layer.

First of all, a glass disk substrate for magnetic disk was made as follows by a press molding method.

By preparing a highly dense sintered columnar body of tungsten carbide (WC) [composition: $WC/Co/Cr_3C_2$ = 91/8/1(wt %)] by 98 mm in diameter and 30 mm in height followed by mirror polish on one bottom surface, a platinum-iridium alloy film of 3 μ m in thickness was formed by use of a high frequency spattering device. After forming the alloy film, sputtering film surface was mirror polished. 2 pieces of tungsten carbide sintered blocks were prepared by coating the mirror finished surface thus made with platinum / iridium alloy. A pair of press dies consisting of 2 platinum-iridium alloy coated tungsten carbide sintered blocks having a mirror finished surface.

By setting a pair of press dies 5 and 6 onto a press machine as shown in Fig. 2, a raw material preheated up to 600°C whose composition is of SiO_2 68wt%, K_2O 8wt%, B_2O_3 11wt%, BaO 2wt%, and Na_2O_3 11wt%, which is a glass circular disk (a circular disk form with 95-0 mm in diameter, 1.21 mm in thickness having a circular hole with 25,0 mm in diameter located at the center area) 7, are disposed between a pair of dies which are heated up to 700°C followed by holding them for 2 minutes so that a clearance becomes 1.20 mm between a pair of dies located at upper and lower positions under pressure of 2 $kgcm^{-2}$, being cooled for 10 minutes down to 450°C with the circular disk form holding the glass material between the dies, and then the glass disk after forming was taken out.

In Fig. 1, numerals 8 and 9 are heating heaters for press dies 5 and 6, numeral 10 is a supply jig for raw material glass circular disk, numeral 11 is a piston cylinder for upper die, numeral 102 is a preheating tunnel furnace for raw material glass circular disk, and numeral 103 is a take-out exit for formed disk. In this manner, a doughnut -shape glass disk substrate 1 was made which has a hole for mounting a rotating shaft on its center.

Oxides comprising Co ferrite film 3 of magnetic thin film for magnetic recording medium and CoZnFe amorphous oxide film layer 2 of its under layer film were formed as follows by a plasma enhanced MO-CVD method on one surface of the glass disk substrate 1 thus made.

Fig. 3 shows a schematic drawing of plasma CVD apparatus to be used for making a magnetic recording medium in one embodiment of the present invention. In the figure, numeral 12 is a reaction chamber, 13 is an electrode, 14 is an exhausting system for keeping the reaction chamber inside a low pressure, 15 is a high frequency electric source (13,56 MHz), numerals 16 - 20 are vaporizers taining raw material therein, numerals 21 - 25 are first valves for controlling the introduction of carrier gas into the carburetors, numerals 26 - 30 are second valves for controlling the introduction of raw material gas and carrier gas into the vaporizers, numeral 31 is a raw material gas and carrier gas cylinder (for nitrogen), numeral 32 is a reaction gas cylinder (for oxygen), and numeral 33 is a substrate heater having a substrate rotating mechanism.

Then, explanation of a production method follows below of magnetic recording medium of the present invention.

Using iron acetylacetonate [$Fe(C_5H_7O_2)_3$], zinc acetylacetonate [$Zn(C_5H_7O_2)_2H_2O$], and cobalt acetylacetonate [$Co(C_5H_7O_2)_3$], as initial raw materials, dehydrated zinc acetylacetonate (for 2 hours at 100°C under vacuum atmosphere) is put into a vaporizer 16, cobalt acetylacetonate is into a vaporizer 17, and iron acetylacetonat into a vaporizer 18, and those materials are respectively k pt at 80 °C, 130 °C and 120 °C with heating. By introducing nitrogen carrier vapor (flow volume of 10 SCCM into vaporizers 16, 17 and 18 respectively)

along with respective acetylacetonate vapors of aforementioned zinc, cobalt, and iron, and oxygen (flow volume 5 SCCM) through op ning th first valves 21 - 23 and second valves 26 - 28 into a depressed reaction chamber 12 which is depressed through an exhaust system 14, a plasma is generated (at power 1,5 W/cm^2), and a film of CoZnFe oxide film 2 is formed on a disk 1 consisting of a glass and the like heated to 400 °C (120 rpm) following a reaction in a depressed pressure (0.08 Torr) for 2 minutes, and then the first valve 21 and the second valve 26 were closed.

Further following the above, the reaction was continued for 9 minutes under the same film forming conditions at a reduced pressure (0.06 Torr), forming a Co ferrite film 3 on the CoZnFe oxide film 2 and also forming such a 2-layer film of Co ferrite / CoZnFe oxide. And, by taking out from the reaction chamber 12 a disk substrate 1 which formed its second layer film, forming 2- layer film of the same , structure on the back side in the same manner, followed by making a Co ferrite / CoZnFe oxide disk having a magnetic thin film on both sides. Then, after giving a heat treatment to this disk for 3 hours in the air at 300 °C followed by applying a lubricant layer 4 to the surfaces through immersion in a liquid bath (not illustrated here) which contains fluorescent organic lubricant, the magnetic recording medium of a magnetic rigid disk form was made.

The magnetic recording medium of the present embodiment thus obtained in such a manner was subjected to evaluation of electromagnetic transfer characteristic with a selected head current value of 50 mA by use of MIG head having a gap length (GL) of 0.25 μ m and truck width (Tw) of 10 μ m. By rotating the magnetic rigid disk at a speed of 3,600 r.p.m., evaluation was made on a circumferential truck at 20.0 mm from the center of the disk. The relative speed between the magnetic rigid disk and the magnetic head were 7.5/sec and a flying height of the magnetic head was 0.15 μm.

For comparison, a conventional Co-Ni / Cr alloy thin film magnetic recording medium was made of a magnetic rigid disk (magnetized orientation in an inner direction of aluminum substrate) form, on which a similar lubricant layer as that of the present invention was provided by forming a carbon film of 600 Å as a protection layer on a magnetic layer whose film thickness is 800 Å and which is consisting of a Co-Ni magnetic layer and Cr layer of Ms=800 emu/cc at Hc=1,0 kOe.

Besides, a magnetic recording medium was made in a magnetic rigid disk form with a Co ferrite thin film without a under lay r film (Co ferrite monolayer medium) whose structure is composed of a Co ferrite magnetic film (the forming conditions are the same as those of the 2-layer film,) formed directly on a glass disk substrate.

Then, the magnetic transfer characteristic was measured in the same conditions as the magnetic recording medium of the present embodiment. Comparisons were made and shown in Fig. 4 of th relationship between the magnetic recording medium of the present embodiment thus obtained in this manner and the conventional Co-Ni / Cr alloy thin film medium, and between the recording density or recording wave length and reproduced output of Co ferrite monolayer medium.

In Fig. 4, the abscissa represents a recording density or recording wave length, while the ordinate represents an output voltage. Besides, in the figure, numeral 34 shows the magnetic recording medium of the present embodiment, numeral 35 shows the conventional Co-Ni / Cr alloy thin film medium for comparison purpose, numeral 36 shows the characteristic of Co ferrite monolayer film medium, respectively.

From Fig. 4, the magnetic recording medium of the present embodiment shows a higher value of output voltage in a high recording density side of a short wave length range than those of the conventional Co-Ni / Cr alloy thin film medium and Co ferrite monolayer layer medium, which clearly demonstrates that the magnetic recording medium of the present embodiment are able to comply with the high recording density.

Still more, observing through an oscilloscope a reproduced wave shape of the recording signal at 500 KHz of the magnetic recording medium of the present invention shows that it represents a dipulse wave shape containing a perpendicular magnetic recording component as its character.

After completing the measurement of the electromagnetic transfer characteristic, an analysis of crystal structure was made through an X-ray diffraction of Co ferrite / CoZnFe oxide magnetic recording medium, excluding the lubricant layer 4 of a magnetic recording medium of the present embodiment by using an organic solvent.

In consequence, it was known that the Co ferrite / CoZnFe oxide magnetic recording medium was composed of a spinel crystal structure and was predominantly orientated to (100).

For comparison purpose, after making a specimen on which film is formed with CoZnFe oxide film2 alone under the same film forming conditions as aforementioned embodiment on a glass disk substrate 1 followed by heat-treating it in the air at 300 °C for 3 hours, an analysis of crystal structure was made through the X-ray diffraction method.In consequ nce, it was found in terms of an the X-ray that th CoZnF oxide film 2 was of a amorphous typ .

Furthermore, as a result of observation on a surface and a broken-out section through the use of a high-resoluti n scanning electron microscope

breaking the Co ferrite monolayer medium of the magnetic layer film medium of the present embodiment and comparison specimen, it was known that the 2-layer film of the magnetic recording medium of the present embodiment has a columnar structure with a columnar diameter of 450 - 550 Å at film thickness of about 3100 Å, and Co ferrite monolayer film medium has a columnar structure with a columnar diameter of 200 - 700 Å at film thickness of about 2,500 Å.

Then, magnetic characteristics of Co ferrite monolayer film medium, COZnFe oxide film 2 and Co ferrite / CoZnFe oxide magnetic recording medium were measured by a vibrating sample magnetometer (VSM). In consequence, the CoZnFe oxide film 2 did not show magnetism, but the magnetic recording medium of Co ferrite / CoZnFe oxide showed excellent squareness compared with the Co ferrite mono-layer medium. The coercive force of Co ferrite / CoZnFe oxide magnetic recording medium has Hc (perpendicular) = 1200 Oe, Hc (parallel) = 780 Oe and Ms was 284 emu/cc.

With these matter, the reason why the magnetic recording medium of the present embodiment shows higher output voltage in a high recording density of a short wave region than that in the Co ferrite monolayer medium is considered that the distribution of columnar diameter becomes smaller compared with the case of Co ferrite monolayer by use of amorphous CoZnFe oxide film as an under layer film, and in consequence squareness of the Co ferrite / CoZnFe oxide magnetic recording medium has improved.

And, as a result of the same investigation made on an oxide which contains at least any one element among the elements of magnesium, calcium, titan, vanadium, manganese, iron, cobalt, nickel, copper, zinc, strontium, niobium, cadmium, and barium, a thin film layer which is evaluated as an amorphous material by an X-ray diffraction method was given the same result with the case of the CoZnFe oxide film 8.

In this manner, according to the aforementioned embodiment, as the amorphous CoZnFe oxide film 2 is formed on a glass disk substrate 1 and the Co ferrite film 3 is formed thereon, magnetic recording medium can be produced which has excellent reliability in endurance and hardness and also renders high density magnetic recording. Furthermore, even in case the disk substrate was of a generally produced glass disk substrate, the same result as aforementioned case was naturally obtained.

Embodiment 2

Fig. 5 shows a structure of magnetic recording medium of a magnetic rigid disk form in th present embodiment of the present invention. In this figure, numeral 1 represent a glass disk substrate, numeral 37 represents NiO under layer film, and 3 represents Co ferrite film, numeral 4 represents a lubricant layer.

First of all, in the same manner as in the embodiment 1, a glass disk substrate 1 was made. By using the same device as in th embodiment 1, the Co ferrite film 3 and NiO under layer film 2 of magnetic recording medium thin film were formed on the surface of glass substrate 1 as mentioned below.

As initial materials, iron acetylacetonate [$Fe(C_5H_7O_2)_3$], nickel acetylacetonate [$Ni(C_5H_7O_2)_2H_2O$], and cobalt acetylacetonate [$Co(C_5H_7O_2)_3$]were used.

Putting dehydrated Ni acetylacetonate (for 2 hours at 100°C under vacuum atmosphere) into a vaporizer 16, cobalt acetylacetonate is into a vaporizer 17, and iron acetylacetonate into a vaporizer 18, and those materials are respectively kept at 180 °C, 130 °C and 120 °C with heating. By introducing nitrogen carrier vapor (flow volume of 30 SCCM) along with the nickel acetylacetonate vapor and oxygen (flow volume of 5 SCCM) into a depressed reaction chamber 12 through an exhaust system 14 with valves 21 and 26 opened, plasma is generated (at power 1,5 W/cm²) and a NiO film is formed on a glass disk substrate (120 rpm) heated at 400 °C following a reaction in a depressed pressure (0.08 Torr) for 5 minutes, and then valve 21 and second valve 26 were closed.

Further following this, by opening valves 22, 23, 27, and 28 within this vacuum condition and then introducing carrier gas (flow rate at 3 SCCM in a vaporizer side 17 and at 8 SCCM in a vaporizer side 18) along with vapors of cobalt acetylacetonate and iron acetylacetonate into a reaction chamber 12, a 2-layer film consisting of Co ferrite / NiO was formed by forming the Co ferrite film 3 on the NiO film 37 through a reaction in a plasma (electric power 1.5 W/cm²) for 10 minutes under depressed condition (0,06 Torr).

Then, taking out a glass disk substrate 1 forming a 2-layer film from a vacuum chamber and also forming the same 2-layer film on the back side in the same manner, a Co ferrite / NiO disk having a magnetic thin film on both sides was made.

Besides, after heat-treating this disk for 3 hours in a 300 °C air atmosphere, a magnetic recording medium of a magnetic rigid disk form was made through application immersed in a liquid tank containing a fluorine-contained organic lubricant.

The magnetic recording medium thus obtained was evaluated of electromagnetic transfer characteristic through use of the same magnetic head as used in the embodiment 1 and in the same manner, For a comparison purpose, the same 2 medium as used in the embodiment 1 were also employed here.

A relationship between recording density and output voltag of magn tic recording medium of the pres nt inventi n thus obtained, Co-Ni / Cr alloy thin film medium and Co ferrite monolayer film medium is shown in Fig. 6.

In Fig. 6, th abscissa represents a recording

density (recording wav l ngth) while the ordinate represents an output voltage. Numeral 38 represents the characteristic of magnetic recording medium of the present invention, numeral 35 represents that f Co-Ni / Cr alloy thin film medium for comparison, and numeral 36 represents that of Co ferrite monolayer film medium for comparison.

In Fig. 6, it became clear that magnetic recording medium of the present invention shows a higher values of output voltage than the conventional Co-Bi / Cr alloy thin film medium and Co ferrite monolayer film medium in a high recording density side of short wave length range. Namely, it was found that the magnetic recording medium of the present invention is able to comply with higher recording density. Besides, observation of an output voltage wave form at 500 KHz of recording signals of the magnetic recording medium of the present invention through an oscilloscope showed a dipulse wave form which contains a perpendicular magnetic recording component as its character.

After completing measurement of electromagnetic transfer characteristic, an analysis of crystal structure through an X-ray diffraction was carried out of Co ferrite / NiO magnetic recording medium using an organic solvent and also removing a lubricant film layer.

In addition, for comparison, an analysis of crystal structure through the X-ray diffraction was carried out by making a specimen formed of a NiO film 38 only on a glass disk substrate 1 under the aforementioned conditions and in the same manner a specimen formed of a Co ferrite film 3 on a glass disk substrate under the aforementioned conditions were respectively.
In consequent, the NiO film 38 formed under the aforementioned conditions was completely oriented to (100) in terms of X-ray.

Besides, by using the (100) completely oriented film of NiO as its under layer, the (100) orientation of the Co ferrite film as a magnetic layer was improved compared with the case at which the film was formed directly on the glass disk being subjected to the influence of crystal orientation of the under layer.

In addition, observation was made on a surface and a broken section of the disk through a high-resolution scanning electron microscope by breaking the Co ferrite / NiO magnetic recording medium. As a result, it has become clear that a 2-layer film of the magnetic recording medium showed a columnar structure with a columnar diameter of 400 - 800 Å at a film thickness of about 4,500 Å. Besides as a result of observation of NiO film 38 and Co ferrite film 3 in the same manner through the scanning lectron microscope, th film thickness of NiO film was about 2,000 Å and that of Co ferrite film was 2,500 Å.

Furthermore, analysis of composition of the Co ferrite / NiO magnetic recording medium through an X-ray micro-analyzer revealed that Co / Fe = 5 / 95 was found.

In addition, measurem nt was mad for magnetic characteristic of the Co ferrite / NiO magnetic recording medium by a vibrating sample magnetometer(VSM). As a result, the coercive force of the magnetic recording medium were Hc (perpendicular) = 1,200 Oe and Hc (parallel) = 780 Oe. Further, the Ms of the Co ferrite / NiO 2-layer film was 275 emu / cc.

With these matters, the reason why the magnetic recording medium of the present invention shows higher output voltage in a high recording density side of a shorter wave length range than the Co ferrite monolayer medium is thought that the use of NiO film 38 of (100) orientation as an under layer increased a (100) orientation of the Co ferrite film 3.

In this connection, it became clear that the under layer film became the magnetic recording medium having the same characteristic as the aforementioned, not only when it was used with NiO, but also when it was with CoO and MnO.

Embodiment 3

Fig. 7 shows a structure of magnetic recording medium of a magnetic rigid disk form of the present embodiment of the present invention. In this figure, numeral 1 represent a glass disk substrate, numeral 39 represents Mn-Zn ferrite thin layer film, numeral 3 represents Co ferrite film, and numeral 4 represents a lubricant layer.

First of all, in the same manner as in the embodiment 1, a glass disk substrate 1 was made. By using the same device as in the embodiment 1, on the surface of this glass substrate 1 the Co ferrite film 3 and Mn-Zn ferrite thin film layer 39 were formed.

Then, explanation follows below of a production method on a magnetic rigid disk of the present embodiment with reference to Fig. 2.

Using iron acetylacetonate $[Fe(C_5H_7O_2)_3]$, Manganese acetylacetonate $[Mn(C_5H_7O_2)_2H_2O]$, Zinc acetylacetonate $[Zn(C_5H_7O_2)_2H_2O]$ and cobalt acetylacetonate $[Co(C_5H_7O_2)_3]$ as initial materials and putting dehydrated manganese acetylacetonate (for 2 hours at 100°C under vacuum atmosphere) into a vaporizer 16, dehydrated Zinc acetylacetonate into a vaporizer 17 (for 2 hours at 100 °C under vacuum atmosphere), cobalt acetylacetonate into a vaporizer 18, and iron acetylacetonate into a vaporizer 19, and those materials are respectively kept at 180 °C, 70 °C, 120 °C and 135 °C with heating.

Opening the 1st valv s 16, 17, and 19 and the 2nd valves 26, 27, and 29, and th n by introducing nitrogen carrier gas (flow v lume of 4 SCCM into the vaporizer 16 side, 7 SCCM into vaporizer 17 side, and 15 SCCM into the vaporizer 19 sid) along with the manganes acetylacetonate vapor, zinc

acetylacetonate vapor, and iron acetylac tonate vapor together with oxygen (flow volume of 5 SCCM) as a reaction gas into a depressed reacti n chamber 12 through an exhaust system 14, plasma is generated (at power 1.5 W/cm²) and a Mn-Zn ferrite film 39 is formed on a glass disk substrate 1 (120 rpm) heated at 400 °C following a reaction in a depressed pressure (0,09 Torr) for 6 minutes, and then the first valve 16 and 17 and second valve 26 and 27 were closed.

Further, following this, by opening the 1st valve 18 and the 2nd valve 28 within this vacuum condition, and then introducing nitrogen carrier gas (flow rate at 8 SCCM) along with vapors of cobalt acetylaceontate and iron acetylacetonate into a reaction chamber 12, a 2-layer film consisting of Co ferrite / Mn-Zn ferrite is formed by forming the Co ferrite film 3 on the Mn-Zn ferrite film 39 through a reaction in a plasma (electric power 1.5 W/cm²) for 8 minutes under depressed condition (0.07 Torr).

Then, taking out a disk substrate 1 forming a 2-layer film from a reaction chamber 12 and also forming the same 2-layer film in the same structure on the back side in the same manner, a Co ferrite / Mn-Zn ferrite disk having a magnetic thin film on both sides was made.

Besides, after heat-treating this disk for 3 hours in a 300 °C air atmosphere, a magnetic recording medium of a magnetic rigid disk form was made by forming a lubricant layer4 through application immersed in a liquid tank containing a fluorine-contained organic lubricant (not illustrated here).

The magnetic recording medium thus obtained was evaluated of electromagnetic transfer characteristic through use of the same magnetic head as used in the embodiment 1 and in the same manner, For a comparison purpose, the same 2 medium as used in the embodiment 1 were also employed here.

A relationship between recording density or recording wave length and output voltage of magnetic recording medium of the present embodiment thus obtained, Co-Ni / Cr alloy thin film medium and Co ferrite monolayer film medium is shown in Fig. 8.

In Fig. 8, the abscissa represents a recording density or recording wave length while the ordinate represents an output voltage. In the figure, numeral 40 represents the characteristic of magnetic recording medium of the present embodiment, numeral 35 represents that conventional of Co-Ni / Cr alloy thin film medium for comparison, and numeral 36 represents that of conventional Co ferrite monolayer film medium for comparison, respectively.

From Fig. 8, it became clear that magn tic recording medium of th present embodiment shows a high r values of utput voltage than the c nventional Co-Ni / Cr all y thin film medium when compared, and in g neral the output volt age is higher than th conventional Co ferrite m nolay r medium when compared, showing that the magnetic recording medium of th present invention is able to comply with higher recording density.,

Besides, observation of an output voltag wave form at 500 KHz of recording signals of the magnetic recording medium of the present embodiment through an oscilloscope showed a dipulse wave form which contains a perpendicular magnetic recording component as its character.

After· completing measurement of electromagnetic transfer characteristic, an analysis of crystal structure through an X-ray diffraction was carried out of Co ferrite / Mn-Zn ferrite 2-layer film by using an organic solvent and then removing a lubricant film layer of the magnetic recording medium of the present, and in consequent, it became clear that the generated film was consisting of a spinel crystal structure with a predominant orientation of (100).

In addition, observation was made on a surface and a broken section of the disk through a high-resolution scanning electron microscope (SEM) by breaking magnetic recording medium of the present embodiment. As a result, it has become clear that the 2-layer film showed a columnar structure with a columnar diameter of 450 - 800 Å at a film thickness of about 3,500 Å. Besides, as a result of observation of Mn-Zn ferrite film 39 and Co ferrite film 3 by making Mn-Zn ferrite film 39 and Co ferrite film 3 as formed on the glass disk substrate 1 for comparison as of served in the same manner through the SEM, the film thickness of Mn-Zn ferrite film was about 1,500 Å and that of Co ferrite film 3 was 2,000 Å. Furthermore, analysis of composition of the Mn-Zn ferrite film 39 and Co ferrite film 3 through an electron beam micro-analyser (EPMA) revealed that Mn / Zn / Fe = 7 / 3 / 20 and Co / Fe = 1 / 19 were respectively found.

In addition, measurement was made for magnetic characteristics of the Mnn-Zn ferrite film 39 and Co ferrite film 3 by a vibrating sample magnetometer (VSM). As a result, the Mn-Zn ferrite film were Hc = 450 Oe and Ms = 325 emu/cc and Co ferrite film were Hc = 1,200 Oe and Ms = 260 emu/cc.

From these matters, the reason why the magnetic recording medium of the present embodiment shows higher output voltage in a high recording density of short wave length range than the conventional Co-Ni / Cr alloy thin film medium is thought that it contains a perpendicular magnetic recoding component, and reason why it shows higher output voltage than Co ferrite monolayer medium is that use of a soft magnetic material as an under layer decreased an influ nce of reversing magn tic field due to generation of a horsesho magnetic circuit with the Co ferrite magnetic layer.

According to the aforementioned embodiment in such a manner, as a Mn-Zn ferrite film 39 is formed n a disk substrate 1 and a cobalt ferrite film 3 is

further formed thereon, a magnetic recording medium can be produced which is capable of high density magnetic recording with excellent reliability for endurance and hardness.

Besides, using the same film forming method as other embodiments of the present invention and forming films of Ni-Zn ferrite, Mn ferrite, Ni ferrite or Zn ferrite as an under layer respectively, and then by making a magnetic recording medium of a magnetic rigid disk form with 2-layer film of Co ferrite / Ni-Zn ferrite, Co ferrite / Mn ferrite, Co ferrite / Ni ferrite or Co ferrite / Zn ferrite, evaluation for electromagnetic transfer characteristic was carried out.

In consequent, in the same case as the magnetic recording medium which consists of a 2-layer film of Co ferrite / Mn-Zn ferrite, a higher output voltage value was shown in a high recording density side of short wave length com pared with the conventional Co-Ni / Cr alloy thin film medium, and a higher output value was shown in general when compared with Co ferrite monolayer medium.

Embodiment 4

Fig. 9 shows a structure of magnetic recording medium of a magnetic rigid disk form of the present embodiment of the present invention. In this figure, numeral 1 represent a glass disk substrate, numeral 2 represents CoZnFe amorphous oxide thin layer file, numeral 40 represents Mn-Zn ferrite thin layer file, numeral 3 represents Co ferrite film, and numeral 4 represents a lubricant layer.

First of all, in the same manner as in the embodiment 1, a glass disk substrate 1 was made. By using the same device as in the embodiment 1, to the surface of this glass disk substrate the Co ferrite film 3, Mn-Zn ferrite film 40, and CoZnFe amorphous oxide thin film 2 were formed.

Then, explanation follows below of a production method on a magnetic rigid disk of the present embodiment.

Using iron acetylacetonate [$Fe(C_5H_7O_2)3$], Manganese acetylacetonate [$Mn(C_5H_7O_2)_2H_2O$], Zinc acetylacetonate [$Zn(C_5H_7O_2)_2H_2O$] and cobalt acetylacetonate [$Co(C_5H_7O_2)_3$] as initial materials and putting dehydrated zinc acetylacetone (for 2 hours at 100°C under vacuum atmosphere) into a vaporizer 16, dehydrated manganese acetylacetonate into a vaporizer 17 (left for 2 hours at 100 °C under vacuum atmosphere), cobalt acetylacetonate into a vaporizer 18, and iron acetylacetonate into a vaporizer 19, and those materials are respectively kept at 75 °C, 180 °C, 120 °C, and 135 °C with heating.

Opening the 1st valves 21, 23, and 14 and the 2nd valves 26, 28, and 29 and then by introducing into a depressed reaction chamber 12 through an exhaust system 14 a nitrogen carrier gas (flow volume of 10 SCCM, respectively) along with acetylacetonate vapor respectively of said zinc, cobalt, and iron together with oxygen (flow volume of 2 SCCM) as a reaction gas, plasma is gen rated (at power 1.5 W/cm²) and a CoZnFe oxide film 2 is form d on a glass disk substrate 1 (120 rpm) heated at 400 °C following a reaction in a depressed pressure (0.10 Torr) for 2 minutes, and then the first valve 23 and second valve 28 were closed.

Following this, by opening the 1st valve 21 and the 2nd valve 26, and then introducing into a reaction chamber 12 depressed by an exhaust system 14 a nitrogen carrier gas (flow rate at 10 SCCM respectively to vaporizers 16, 17 and 19) along with vapors of zinc acetylacetonate, manganese acetylacetonate and iron acetylacetonate together, with oxygen (flow rate 5 SCCM) as a reactive gas, plasma is generated (electric power 1,5 W/cm²) for 5 minutes under depressed condition (0,09 Torr) and a Mn-Zn ferrite film 39 is formed by formed on a disk substrate 1 (120 rpm) with heating at 400 °C, and then the 1st valves 21 and 22 and the 2nd valves 26 and 27 are closed.

Further following this, by opening the 1st valve 23 and the 2nd valve 28, then allowing nitrogen carrier gas (flow rate at 10 SCCM into vaporizers 18 and 19 respectively) along with vapors of cobalt acetylacetonate and iron acetylacetonate together with oxygen (flow rate at 5 SCCM) as a reactive gas to react in a plasma (electric power 1,5 W/cm²) for 8 minutes under depressed condition (0,07 Torr), a 3-layer film consisting of Co ferrite / MN-Zn ferrite film / CoZnFe oxide was formed by putting a Co ferrite film 3 on the Mn-Zn ferrite film 39.

Then, taking out a glass disk substrate 1 forming a 3-layer film from a reaction chamber 12 and also forming the same 3-layer film on the back side in the same manner, a Co ferrite / Mn-Zn ferrite / CoZnFe oxide disk having a magnetic thin film on both sides was made.

Besides, after heat-treating this disk for 3 hours in a 300 °C air atmosphere, a magnetic recording medium of a magnetic rigid disk form was made by forming a lubricant layer4 through application immersed in a liquid tank (not illustrated here) containing a fluorine-contained organic lubricant.

The magnetic recording medium thus obtained was evaluated of electromagnetic transfer characteristic through use of the same magnetic head as used in the embodiment 1 and in the same manner, For a comparison purpose, the same 2 medium as used in the embodiment 1 were also employed here.

A relationship between output voltage and recording d nsity or recording wave length of respective medium is shown in Fig. 10 for comparison.

In Fig. 10, numeral 41 represents th characteristics of the magnetic recording medium of the present embodiment, numeral 35 represents that

of conventional Co-Ni / Cr alloy thin film medium for comparison, and numeral 36 likewise represents that of ther conventi nal Co ferrite monolay r medium.

In Fig. 10, it became clear that magnetic recording medium of the present embodiment shows a higher values of output voltage in general than the conventional Co-Ni / Cr alloy thin film medium by comparison, and it was found that the magnetic recording medium was able to comply with higher recording density.

Besides, observation of an output voltage wave form at 500 KHz of recording signals for the magnetic recording medium of the present embodiment through an oscilloscope showed a dipulse wave form which contains a perpendicular magnetic recording component as its character.

After completing measurement of electromagnetic transfer characteristic, by making a 2-layer film respectively consisting of CoZnFe oxide film 2, Co ferrite film 3, Mn-Zn ferrite film 39 or Mn-Zn ferrite / Co ferrite in the same condition as in the aforementioned embodiment on a glass disk substrate 1 for comparison, an analysis was carried out with a magnetic recording medium which consists of a 3-layer film of Co ferrite / Mn-Zn ferrite / CoZnFe oxide.

First of all, as a result of an analysis made of a crystal structure of the CoZnFe oxide film used as an under layer through an X-ray diffraction method, the CoZnFe oxide film 2 made under the aforementioned conditions was amorphous in terms of an X-ray.

In addition, observation was made on a surface and a broken section of the magnetic rigid disk through a high-resolution scanning electron microscope (SEM) by breaking a magnetic recording medium consisting of a 3-layer film of Co ferrite / Mn-Zn ferrite / CoZnFe oxide. As a result, it has become clear that this 3-layer film showed a columnar structure with a columnar diameter of 500 - 600 Å at a film thickness of about 4,100 Å.

Besides, as a result of observation of a 2-layer film of Co ferrite / Mn-Zn ferrite through the SEM, the film thickness was about 3,500 Å , which shows its columnar growth and the columnar diameter was 450 - 800 Å. Namely, it can be seen that forming an amorphous CoZnFe oxide film 2 as an under layer film makes an average columnar diameter of magnetic layer which consists of the Co ferrite film 3 smaller as well as distribution in its size smaller.

Furthermore, analysis of composition of the Mn-Zn ferrite film 39 and Co ferrite film 3 through an election beam micro-analyser (EPMA) revealed that Mn / Zn / Fe = 7 / 3 / 20, and Co / Fe = 1 / 19 were respectively found.

In addition, measurement was made for magnetic characteristic of a 2-layer film of Mn-Zn ferrite film / CoZnFe oxid film and Co ferrite film 3 by a vibrating sample magnetometer (VSM). As a result, th 2-lay r film of Mn-Zn ferrite film / CoZnFe oxide were; Hc = 20 Oe, Ms = 320 mu / cc, Co ferrite film 3 were Hc = 1,200 O and Ms = 274 emu / cc.

The reason why the magnetic recording medium of the present embodiment shows a higher output voltage in a high recording density side of short wave length region than the Co-Ni / Cr alloy thin film medium is thought that it contains a perpendicular magnetic recording component, and also the reason why it shows higher output voltage than Co ferrite monolayer medium is that use of a soft magnetic material of Mn-Zn ferrite film 39 decreased an influence of reversing magnetic field due to generation of a horse-shoe magnetic circuit with the Co ferrite magnetic layer.

According to the aforementioned embodiment in such a manner, by forming an amorphous CoZnFe oxide film 2 on the disk substrate 1 and also the Mn-Zn ferrite film 39 thereon, the Co ferrite layer 3 forms a columnar Structure thereon in a perpendicular direction to the surface of disk substrate 1; therefore, a magnetic rigid disk having the ability to carry out high density magnetic recording can be produced with excellent reliability for endurance and hardness.

Besides, as a result of the same investigation about the oxide which contains various elements as in the embodiment 1 as an amorphous oxide thin film, and also about various ferrite in the same as in the embodiment 3 as a soft magnetic iron oxide thin film, in the same case as the magnetic recording medium consisting of a 3-layer film of Co ferrite / Mn-Zn ferrite / CoZnFe oxide of the present embodiment, a higher value of output voltage was shown in general compared with the conventional Co-Ni / Cr alloy thin film medium and Co ferrite monolayer medium.

Embodiment 5

Fig.11 shows a structure of magnetic recording medium of a magnetic rigid disk form of the present embodiment of the present invention. In this figure, numeral 1 represents a glass disk substrate, numeral 37 represents a NiO thin film layer, numeral 39 represents a Mn-Zn ferrite thin film layer, numeral 3 represents a Co ferrite film, and numeral 4 represents a lubricant layer.

First of all, a glass disk substrate 1 was made in the same manner as in the embodiment 1. By using the same device as used in the embodiment 1, the Co ferrite film 3, Mn-Zn ferrite film 39, and NiO thin film 37 were formed in the glass substrate 1.

Then, explanation follows below of a production method on a magnetic rigid disk of the present embodiment with reference to Fig. 2.

As initial materials, using iron acetylacetonate [F $(C_5H_7O_2)_3$], Manganese acetylacetonate [$Mn(C_5H_7O_2)_2H_2O$], Zinc acetylacetonate [$Zn(C_5H_7O_2)_2H_2O$] and nick l acetylacetonate [$Ni(C_5H_7O_2)_2H_2O$], and Cobalt acetylacetonate [$Co(C_5H_7O_2)_3$] and putting

dehydrated nickel acetylacetonate (for 2 hours at 100 °C under vacuum atmosph re) into a vaporizer 16, dehydrated manganese acetylacetonate into a vaporizer 17 (for 2 hours at 100 °C under vacuum atmosphere), zinc acetylacetonate into a vaporizer 18 (for 2 hours at 100 °C under vacuum atmosphere), cobalt acetylacetonate into a vaporizer 19, and iron acetylacetonate into a vaporizer 20, and those materials are respectively kept
at 170 °C, 180 °C, 70 °C, 120 °C, and 135 °C with heating.

Opening the 1st valve 21 and the 2nd valve 26, and then by introducing into a depressed reaction chamber 12 through an exhaust system 12 a nitrogen carrier gas (flow volume of 20 SCCM) along with nickel acetylacetonate vapor together with oxygen (flow volume of 3 SCCM) as a reaction gas, plasma is generated (at power 1,5 W/cm²) and a NiO film 37 is formed on a glass disk substrate 1 (120 rpm) heated at 400 °C following a reaction at a depressed pressure (0.10 Torr) for 4 minutes, and then the first valve 21 and second valve 26 were closed.

Following this, by opening the 1st valves 22, 23, and 25, and the 2nd valves 27, 28, and 30 in a vacuum atmosphere, and then introducing into a reaction chamber 12 depressed by an exhaust system 14 nitrogen a carrier gas (flow rate at 4 SCCM to vaporizer 17, flow rate at 7 SCCM to vaporizer 18, and flow rate at 15 SCCM to vaporizer 20,) along with vapors of manganese acetylacetonate, zinc acetylacetonate and iron acetylacetonate together with oxygen (flow rate 5 SCCM) as a reactive gas, plasma is generated (electric power 1.5 W/cm²) for 6 minutes under depressed condition (0.09 Torr) and a Mn-Zn ferrite film 39 is formed on a disk substrate 1 (120 rpm) following heating to 400 °C, and then the 1st valves 22 and 23 and the 2nd valves 27 and 28 are closed.

Further following this, by opening the 1st valve 24 and the 2nd valve 29 within a vacuum atmosphere, and introducing nitrogen carrier gas (flow rate at 7 SCCM into vaporizers) along with cobalt acetylacetonate vapor and iron acetylacetonate vapor into a reactive chamber 12, allowing them to react in a plasma (electric power 1,5 W/cm²) for 8 minutes under depressed condition (0,07 Torr), a 3-layer film consisting of a Co ferrite / Mn-Zn ferrite film / NiO is formed by putting a Co ferrite film 3 on the Mn-Zn ferrite film 39.

Then, taking out a glass disk substrate 1 which forms a 3-layer film from a reaction chamber 12, and also forming the same 3-layer film on the back side in the same manner, a Co ferrite / Mn-Zn ferrite disk / NiO disk having a magnetic thin film on both sides was made.

Besides, after heat-treating this disk for 3 hours in a 300 °C air atmosphere, a magnetic recording medium of a magnetic rigid disk form was made by forming a lubricant layer 4 through an application immersed in a liquid tank (not illustrated here) containing a fluorine-contained organic lubricant.

The magnetic recording medium thus obtained was evaluated of electromagnetic transfer characteristic through use of the same magnetic head as used in the embodiment 1 and in the same manner. As a comparison specimen, the same 2 medium as used in the embodiment 1 were also employed here.

A relationship between output voltage and recording density or recording wave length of respective medium is shown in Fig, 12 for comparison.

In Fig. 12, numeral 42 represents characteristic of the magnetic recording medium of the present embodiment, numeral 35 represents that of the conventional Co-Ni / Cr alloy thin film medium for comparison, and numeral 36 likewise represents that of the conventional Co ferrite monolayer medium, respectively.

From Fig. 12, it became clear that magnetic recording medium of the present embodiment shows a higher values of output voltage in general than the conventional Co-Ni / Cr alloy thin film medium, and Co ferrite monolayer medium by comparison, and it was found that the magnetic recording medium was able to comply with higher recording density.

Besides, observation of an output voltage wave form at 500 KHz of recording signals of the magnetic recording medium of the present embodiment through an oscilloscope showed a dipulse wave form which contains a perpendicular magnetic recording component as its character.

After completing measurement of electromagnetic transfer characteristic, as a result of observation was on a surface and a broken section of the magnetic recording medium of the present embodiment following the breaking thereof through a high-resolution scanning electron microscope (SEM), it has become clear that this 3-layer film showed a columnar structure with a columnar diameter of 500 - 900 Å at a film thickness of about 4,500 Å.

By making a NiO film 37, a Mn-Zn ferrite film 39 and Co ferrite film 3 in the same conditions as in the aforementioned embodiment on the glass disk substrate for comparison, as a result of observation through the SEM in the same manner, the film thickness was about 1,000 Å for NiO film 37, about 1,500 Å for Mn-Zn ferrite film 39, and about 2,000 Å for Co ferrite film 3.

Furthermore, analysis of composition of the Mn-Zn ferrite film 39 and Co ferrite film 3 through an X-ray micro-analyser (EPMA) revealed that Mn / Zn / Fe = 7 / 3 / 20, and Co / F = 1 / 19 were respectively found.

In additi n, measurement was made for magnetic characteristic of the Mn-Zn ferrite film 39 and Co ferrite film 3 through a vibrating sampl

magnetometer (VSM). As a result, the Mn-Zn ferrite film 39 was Hc = 45 Oe, Ms = 320 emu / cc, Co ferrite film 3 were Hc = 1,200 Oe and Ms = 280 emu / cc.

Besides, an analysis of crystal structure through the X-ray diffraction was carried out of a NiO film 37 used for an under layer had a complete orientation to (100) of NaCl type crystal structure, and the orientation of (100) for any of Mn-Zn ferrite film 39 and Co ferrite film 3 had been improved in a spinel crystal structure compared with a case when an under layer is not provided under the influence of the orientation of NiO film 37.

The reason why the magnetic recording medium of the present embodiment shows a higher output voltage in a high recording density side of a short wave length area than the Co-Ni / Cr alloy thin film medium is thought that it contains a perpendicular magnetic recording component, and also the reason why it shows higher output voltage than Co ferrite monolayer medium is that use of a soft magnetic material as Mn-Zn ferrite film decreased an influence of reversing magnetic field due to generation of a horseshoe magnetic circuit with the Co ferrite magnetic layer.

According to the aforementioned embodiment thus indicated above, as the NiO film 37 is formed on the disk substrate 1, the Mn-Zn ferrite film 39 thereon, and the Co ferrite layer 3 is further formed thereon, a magnetic rigid disk having the ability to carry out high density magnetic recording with excellent reliability for endurance and hardness.

Besides, by making a 3-layer film medium with use of CaO or MnO made in the same manner as in the embodiment 2 in place of NiO film 37, and various kinds of ferrite ob tained in the same manner as in the embodiment 3 in place of Mn-Zn ferrite film 39 as a soft magnetic iron oxide thin film, as a result of the evaluation on the electromagnetic transfer characteristic, a higher value of output voltage was shown in general compared with the conventional Co-Ni / Cr alloy thin film medium in the same case as the magnetic recording medium consisting of a 3-layer film of Co ferrite / Mn-Zn ferrite / NiO of the present embodiment.

Claims

1. A magnetic recording medium, comprising: an oxide thin film layer arranged on a surface of a disk substrate; a columnar structural film formed with columnar grains which stand perpendicularly and furthermore thickened to said disk substrate surfac on said layer; a ferromagnetic iron oxide thin film layer containing cobalt which is identified as a spinel crystal structure by an X-ray diffracti n method; and a structure arranged with a lubricant layer further thereon.

2. A magnetic recording medium as claim d in claim 1, in which th oxide thin film layer is a thin film layer identified as an amorphous material by an X-ray diffraction method.

3. A magnetic recording medium as claimed in claim 1, in which the oxide thin film layer is an oxide thin film layer of NaCl crystal structure.

4. A magnetic recording medium as claimed in claim 1, in which the oxide thin film layer is a soft magnetic iron oxide thin film layer of a spinel crystal structure.

5. A magnetic recording medium as claimed in claim 1, in which the oxide thin film layer comprises a 2-layer film of oxide having such a structure that a soft magnetic iron oxide thin film layer of spinel crystal structure is laminated on a thin film layer identified as an amorphous material by an X-ray diffraction method.

6. A magnetic recording medium as claimed in claim 1, in which the oxide thin film layer is a 2-layer film of oxide having a structure in which soft magnetic iron oxide thin film layer of spinel crystal structure is laminated on an oxide thin film layer of NaCl crystal structure.

7. A magnetic recording medium as claimed in claim 1, in which a disk substrate is a disk-shape glass substrate produced with use of a press molding by heating a glass material.

8. A magnetic recording medium as claimed in claim 2, in which the thin film layer identified as an amorphous material by an X-ray diffraction method contains at least one element out of such a group of elements as magnesium, calcium, titanium, vanadium, manganese, iron, cobalt, nickel, copper, zinc, strontium, niobium, cadmium, and barium.

9. A magnetic recording medium as claimed in claim 1, in which the oxide thin film layer of NaCl crystal structure is a film predominantly oriented to (100) crystallographically and comprises at least any one of the following oxides, NiO, CoO, and MnO.

10. A magnetic recording medium as claimed in claim 4, in which the soft magnetic iron oxide thin film layer of spinel crystal structure comprises an iron oxide which contains at least any one element out f a group of elem nts as zinc, manganese, and nickel.

11. A magnetic recording medium as claimed in claim 5, in which the thin film layer id ntified as an

amorphous material by an X-ray diffraction method contains at least any on element out of such a group of elements as magnesium, calcium, titanium, vanadium, manganese, iron, cobalt, nickel, copper, zinc, strontium, niobium, cadmium, and barium.

12. A magnetic recording medium as claimed in claim 5, in which the soft magnetic iron oxide thin film layer of spinel crystal structure comprises an iron oxide which contains at least any one element out of a group of elements as zinc, manganese, and nickel.

13. A magnetic recording medium as claimed in claim 6, in which the oxide thin film layer of NaCl crystal structure is a film predominantly oriented to (100) crystallographically and comprises at least any one of the following oxides, NiO, CoO, and MnO.

14. A magnetic recording medium as claimed in claim 6, in which the soft magnetic iron oxide thin film layer of spinel crystal structure comprises an iron oxide which contains at least any one element out of a group of elements as zinc, manganese, and nickel.

15. A production method of a magnetic recording medium in which, by using a mixture of gases comprising a vapor of at least any one organic metallic compound out of a group of respective organic metallic compound which contains each element of magnesium, calcium, titanium, vanadium, manganese, iron, cobalt, nickel, copper, zinc, strontium, niobium, cadmium, and barium and an oxygen, a chemical deposition is made on a substrate in a plasma followed by making an oxide thin film layer identified as an amorphous material by an X-ray diffraction method, and further a ferromagnetic iron oxide thin film layer containing cobalt is made on its surface by chemically depositing in a plasma a mixture of gases consisting of a vapor of organic metallic compound which contains iron, a vapor of organic metallic compound which contains cobalt, and oxygen.

16. A production method of a magnetic recording medium in which, by using a mixture of gases comprising a vapor of at least any one organic metallic compound out of a group of respective organic metallic compound which contains each element of nickel, cobalt and manganese and an oxygen, a chemical deposition is made on a substrate in a plasma followed by making a oxide thin film layer of NaCl crystal structure, and further a ferromagnetic iron oxid thin film layer containing cobalt is made on its surface by chemically depositing in a plasma a mixture of gases consisting of a vapor of organic metallic compound which contains iron, a vapor of organic metallic compound which contains cobalt, and oxygen.

17. A production method of a magnetic recording medium in which, by using a mixture of a gases comprising a vapor of at least any one organic metallic compound out of a group of respective organic metallic compound which contains each element of zinc, manganese, and nickel, a vapor of organic metallic compound which contains iron, and an oxygen, a chemical deposition is made on a substrate in a plasma followed by making a soft magnetic iron oxide thin film layer of spinel crystal structure, and further a ferromagnetic iron oxide thin film layer containing cobalt is made on its surface by chemically depositing in a plasma a mixture of gases consisting of a vapor of organic metallic compound which contains iron, a vapor of organic metallic compound which contains cobalt, and oxygen.

18. A production method of a magnetic recording medium in which, by using a mixture of gases comprising a vapor of at least any one organic metallic compound out of a group of respective organic metallic compound which contains each element of magnesium, calcium, titanium, vanadium, manganese, iron, cobalt, nickel, copper, zinc, strontium, niobium, cadmium, and barium, and an oxygen, a chemical deposition is made on a substrate in a plasma followed by making an oxide thin film layer identified as an amorphous material by an X-ray diffraction method; and further a soft magnetic iron oxide thin film layer of spinel crystal structure is made on its surface by chemically depositing in a plasma and using a mixture of gases consisting of a vapor of organic metallic compound which contains iron, a vapor of organic metallic compound which contains at least any one organic metallic compound out of a group of respective organic metallic compounds which contain each element of zinc, manganese, and nickel, and an oxygen; and furthermore a ferromagnetic iron oxide thin film layer containing cobalt is made on its surface by chemically depositing in a plasma a mixture of gases consisting a vapor of organic metallic compound which contains iron, a vapor of organic metallic compound which contains cobalt, and oxygen.

19. A production method of a magnetic recording medium in which, by using a mixture of a gases comprising a vapor of at least any one organic

metalli compound out of a group of respective rganic metallic compound which contains each elem nt of nickel, cobalt, and manganese, and an oxygen, a chemical d position is made on a substrate in a plasma followed by an oxide making a thin film layer of a naCl crystal structure; and further a soft magnetic iron oxide thin film layer of spinel crystal structure is made on its surface by chemically depositing in a plasma and using a mixture of gases consisting of a vapor of organic metallic compound which contains iron, a vapor of organic metallic compound which contains at least any one organic metallic compound out of a group of respective organic metallic compounds which contain each element of zinc, manganese, and nickel, and an oxygen; and furthermore a ferromagnetic iron oxide thin film layer containing cobalt is made on its surface by chemically depositing in a plasma a mixture of gases consisting of a vapor of organic metallic compound which contains iron, a vapor of organic metallic compound which contains cobalt, and oxygen.

FIG. 1

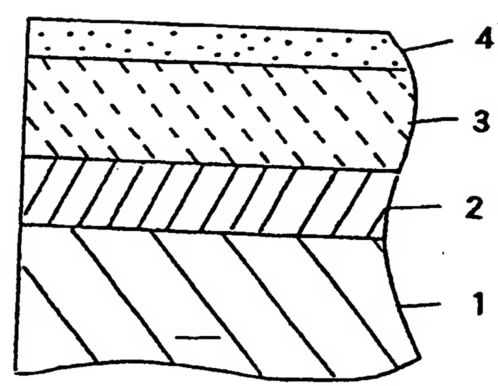
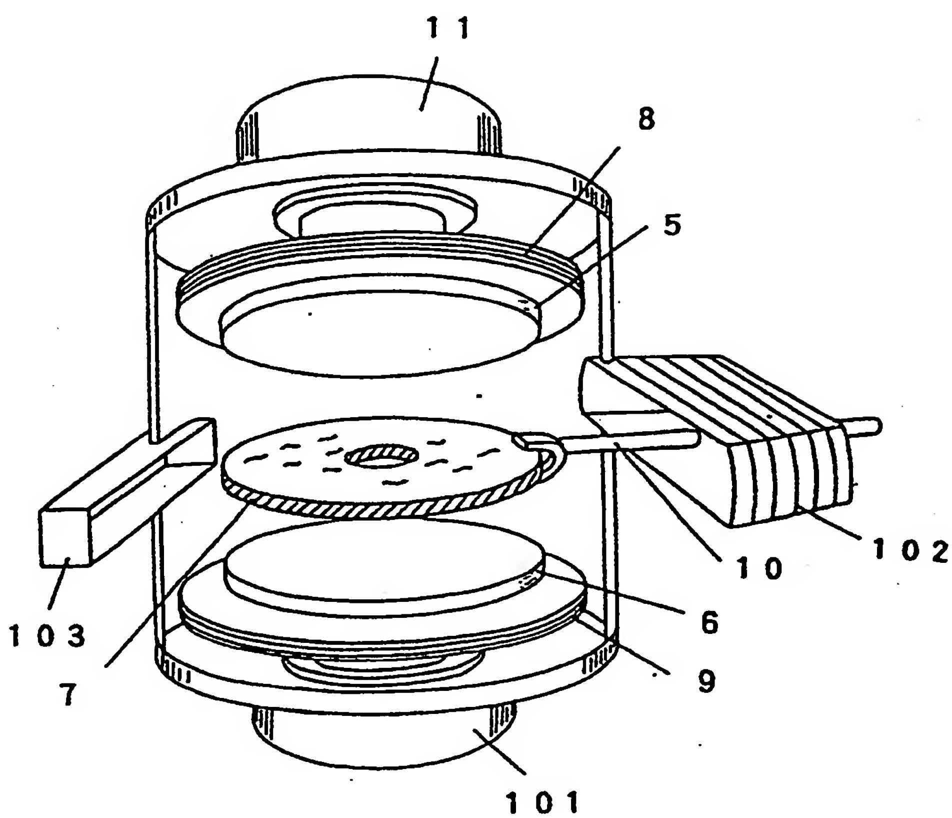


FIG.2



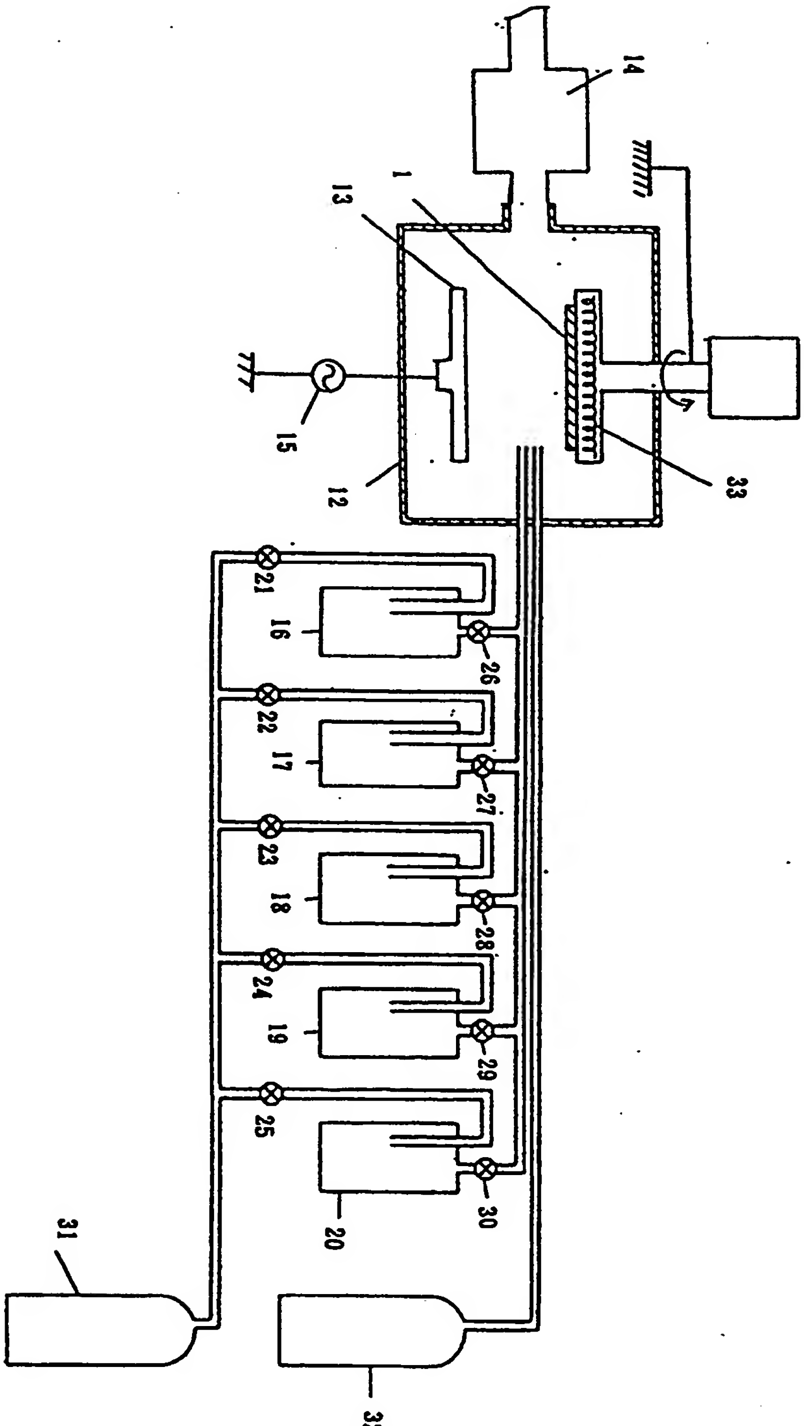


FIG.3

FIG.4

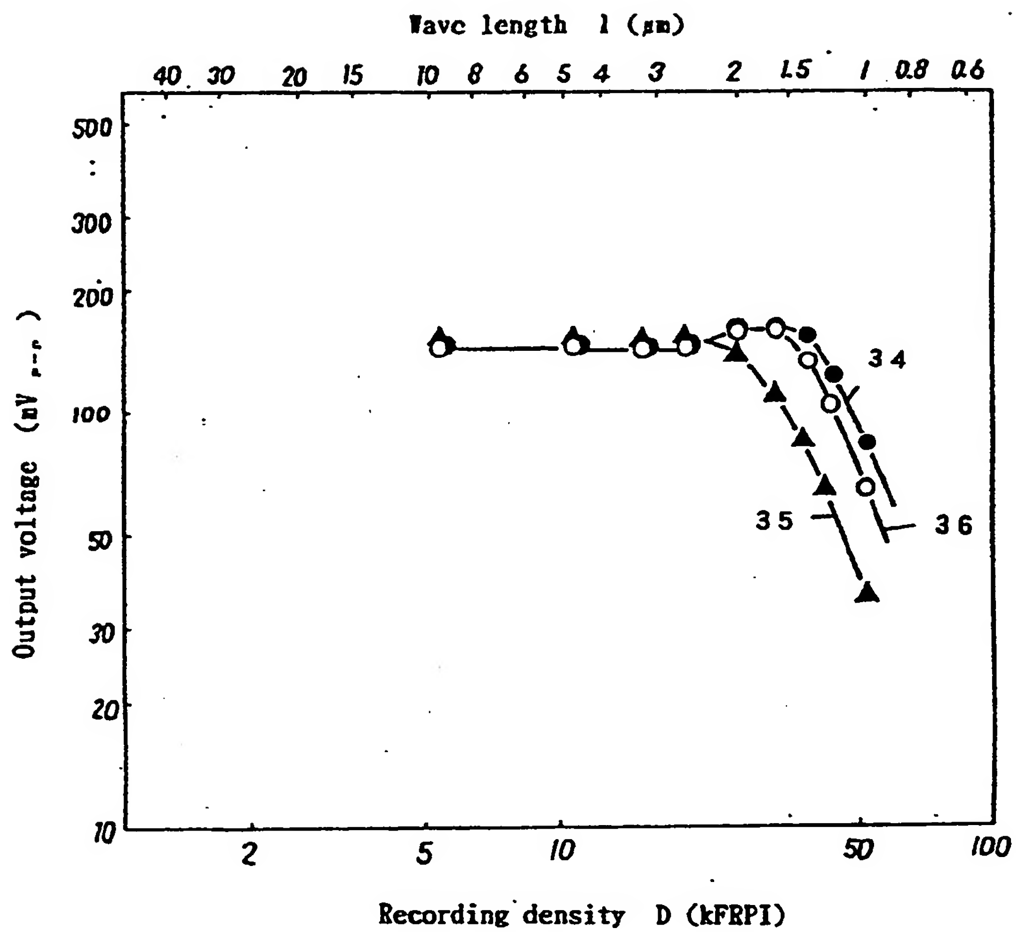

Wave length l (μm)
40 30 20 15 10 8 6 5 4 3 2 1.5 1 0.8 0.6
500
300
200
100
50
30
20
10
Output voltage (mV p-p)
34
35
36
2 5 10 50 100
Recording density D (kFRPI)

FIG.5

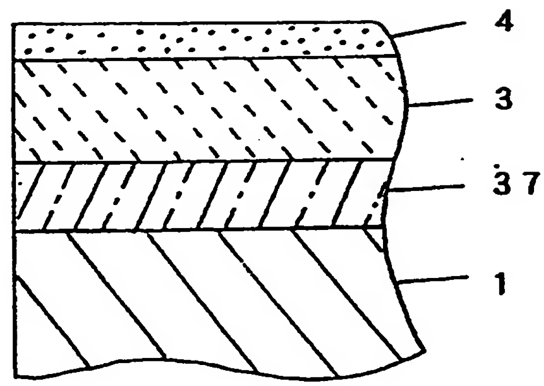


FIG.6

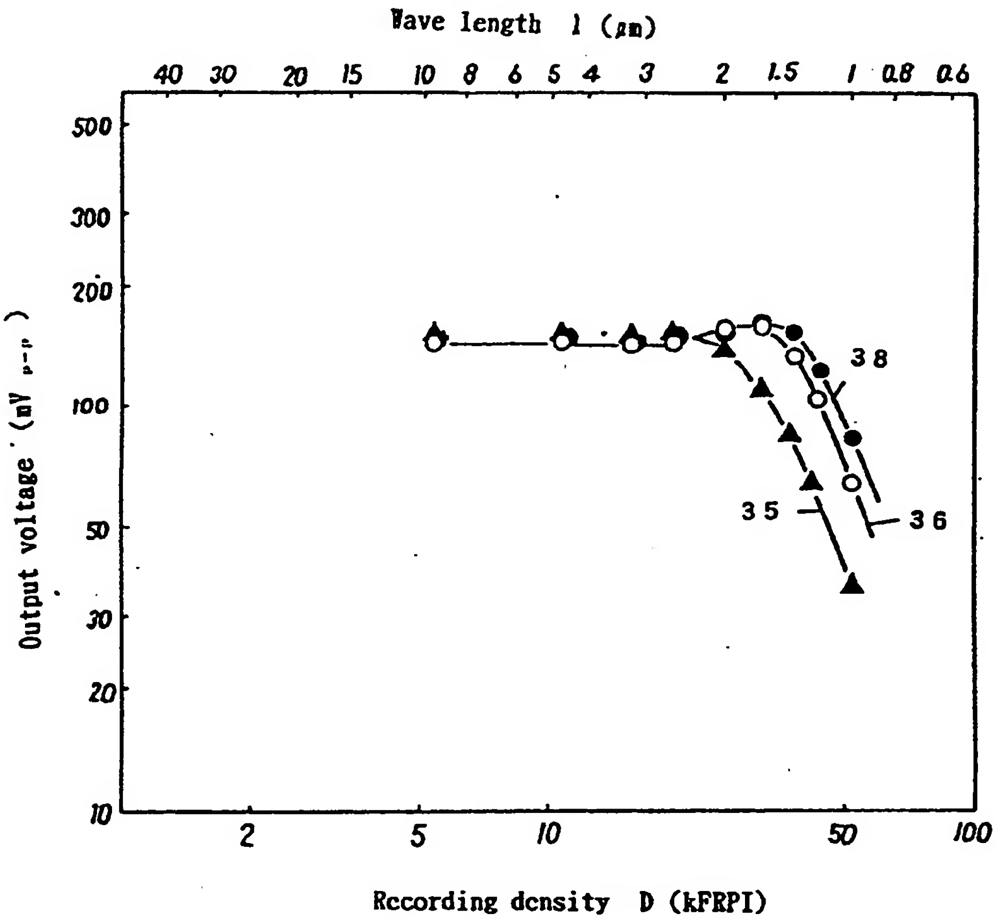

Wave length l (μm)
40 30 20 15 10 8 6 5 4 3 2 1.5 1 0.8 0.6
500
300
200
100
50
30
20
10
Output voltage (mV p-p)
2 5 10 50 100
Recording density D (kFRPI)
38
35
36

FIG.7

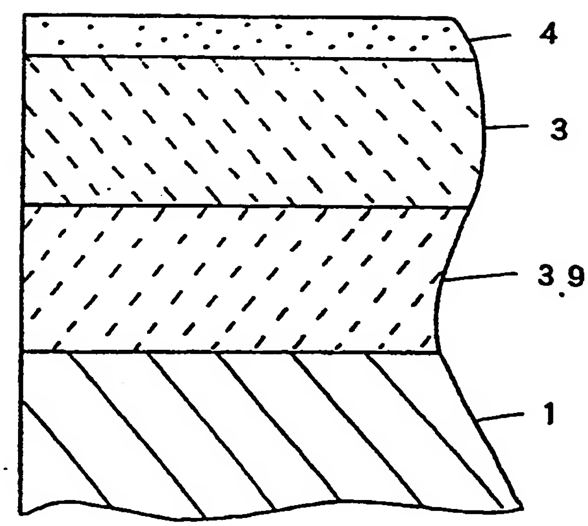


FIG.8

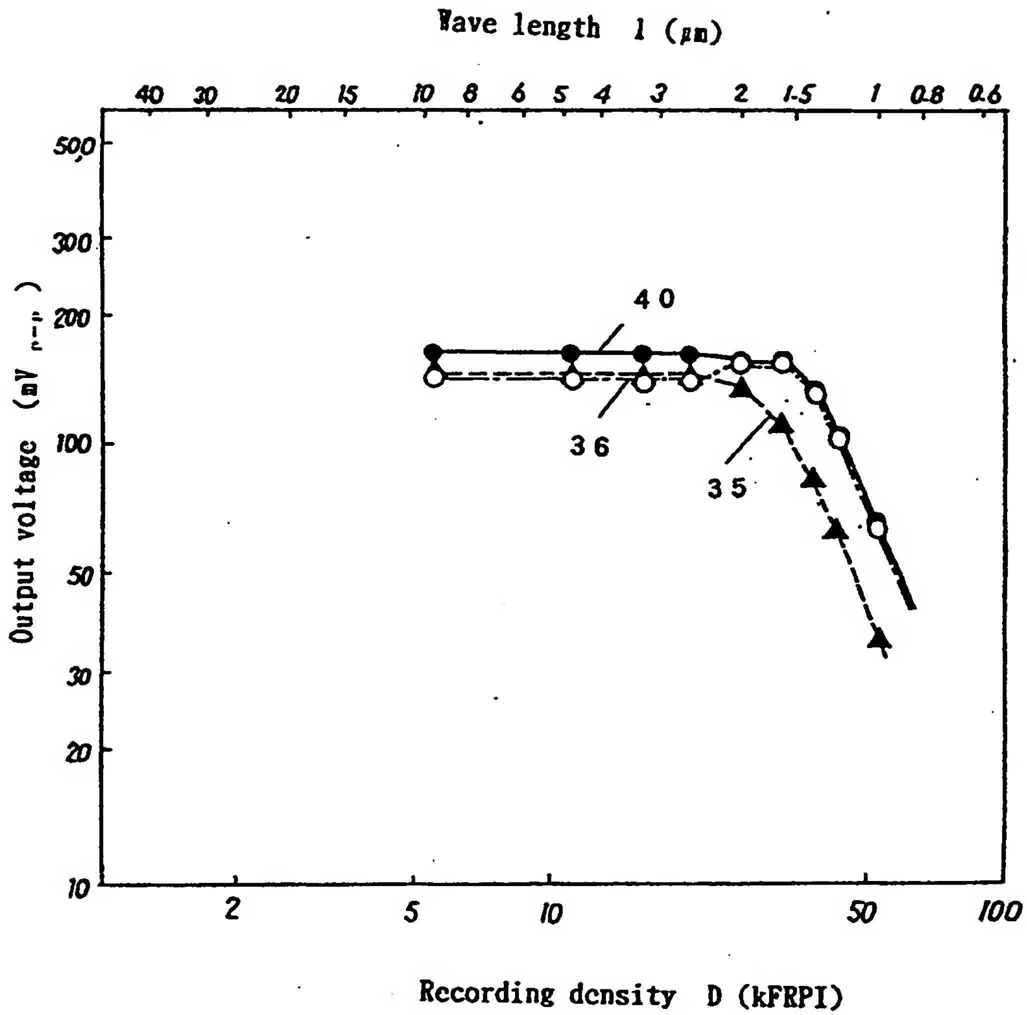

Wave length l (μm)
40 30 20 15 10 8 6 5 4 3 2 1.5 1 0.8 0.6
500
300
200
100
50
30
20
10
Output voltage (mV p-p)
40
36
35
2
5
10
50
100
Recording density D (kFRPI)

FIG.9

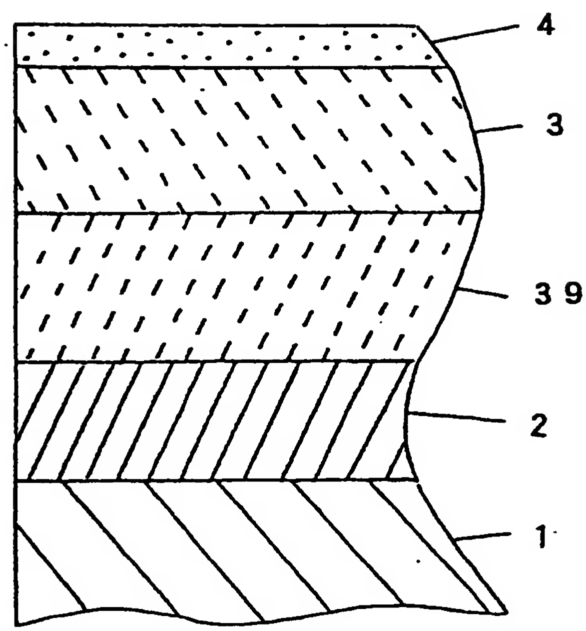


FIG. 10

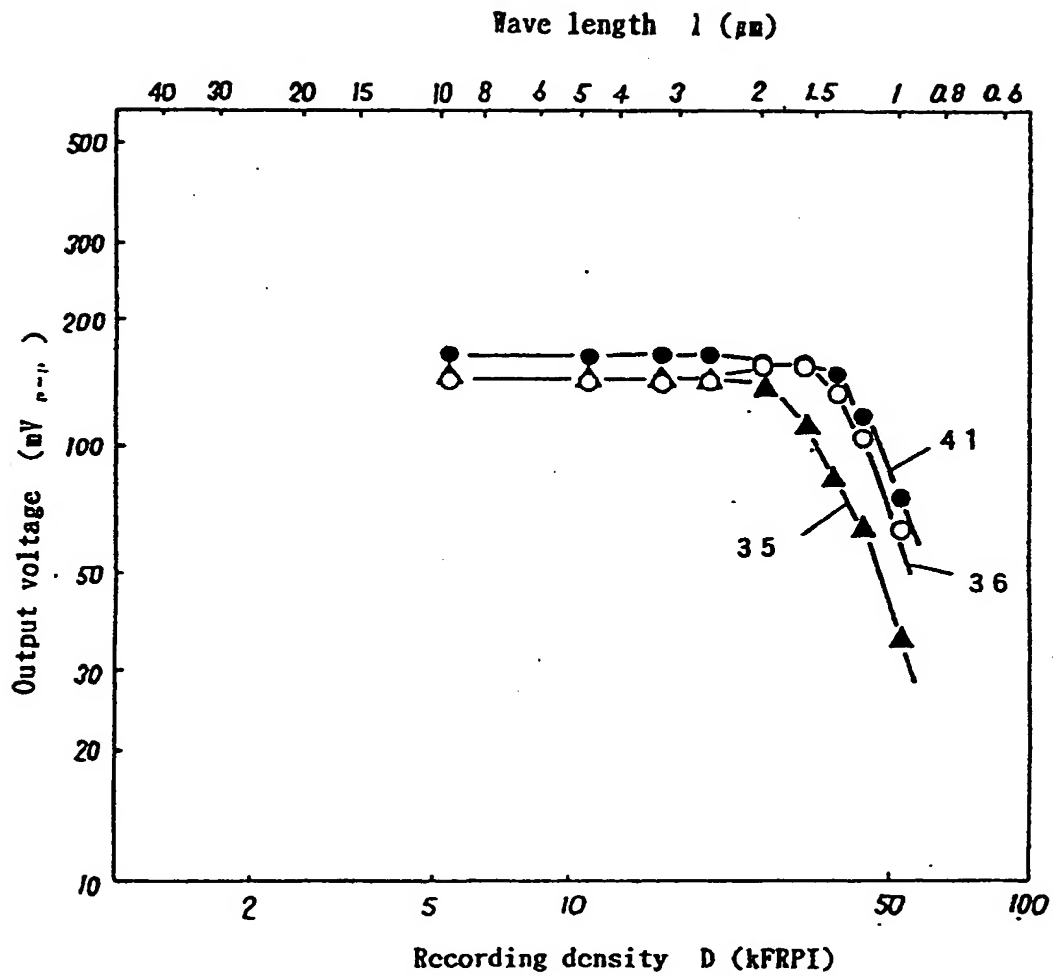

Wave length l (μm)
40 30 20 15 10 8 6 5 4 3 2 1.5 1 0.8 0.6
500
300
200
100
50
30
20
10
Output voltage (mV p-p)
41
35
36
2 5 10 50 100
Recording density D (kFRPI)

FIG.11

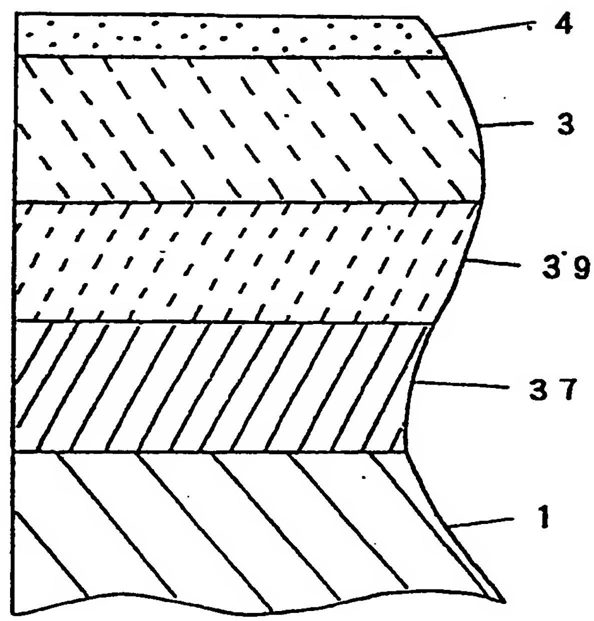
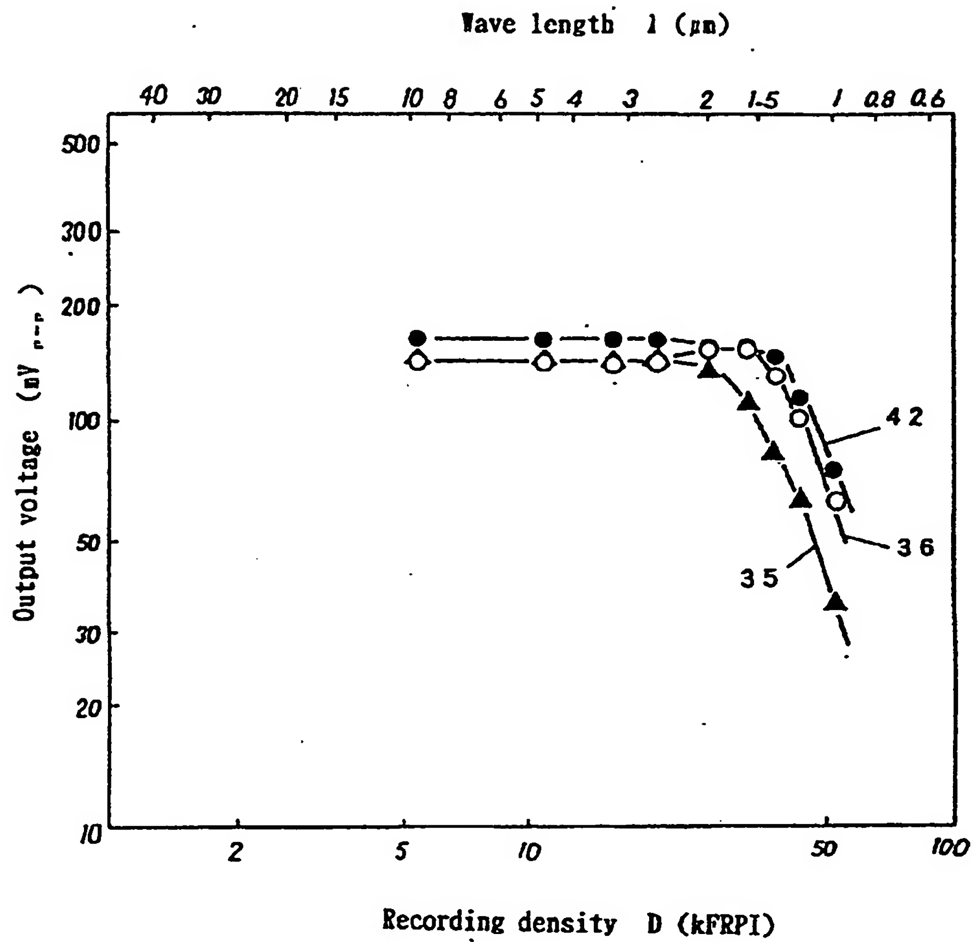


FIG.12


Wave length l (μm)
40 30 20 15 10 8 6 5 4 3 2 1.5 1 0.8 0.6
500
300
200
100
50
30
20
10
Output voltage (mV p-p)
42
36
35
2
5
10
50
100
Recording density D (kFRPI)